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Rare Earth Recycling and the Balance Problem

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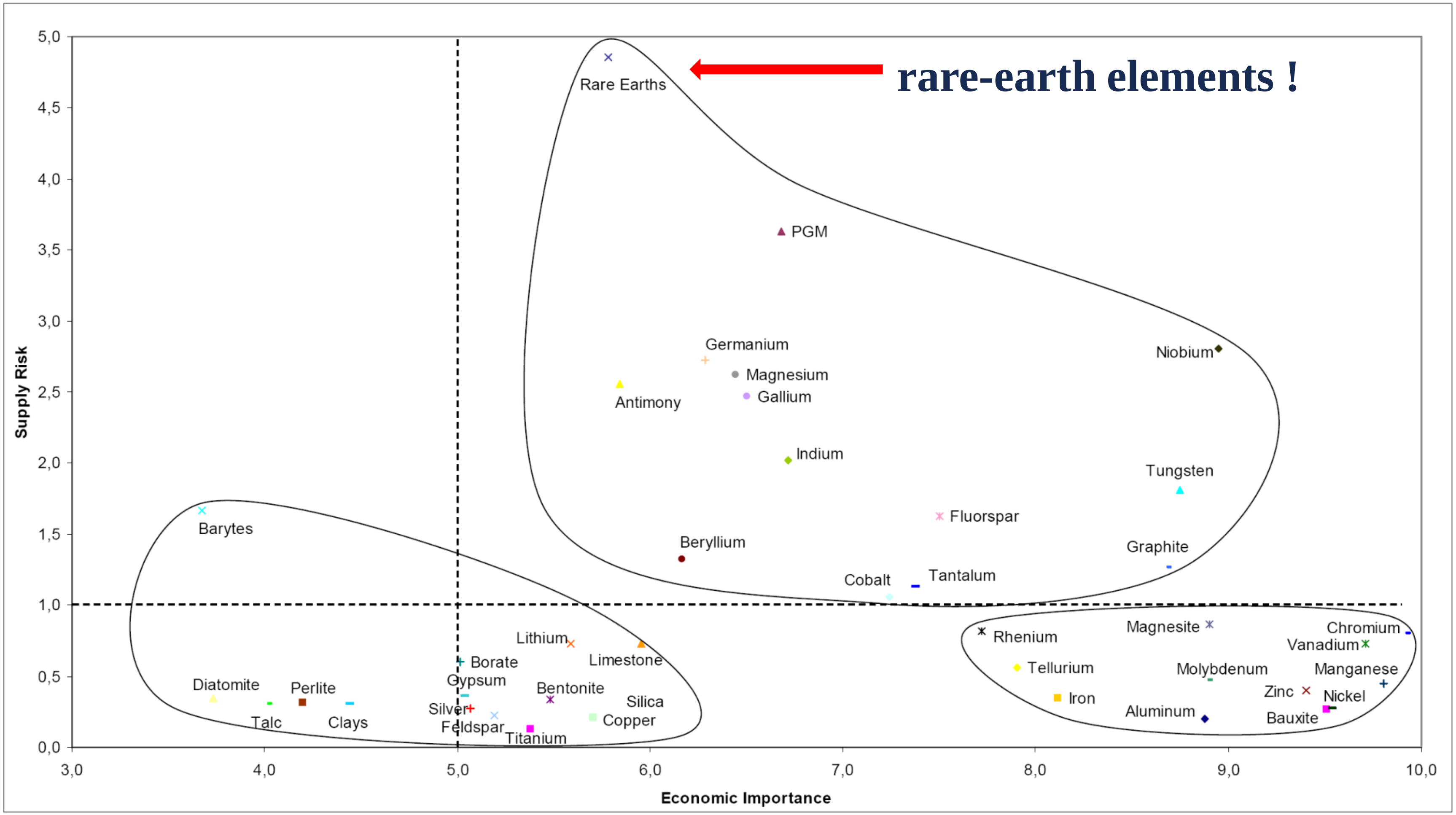
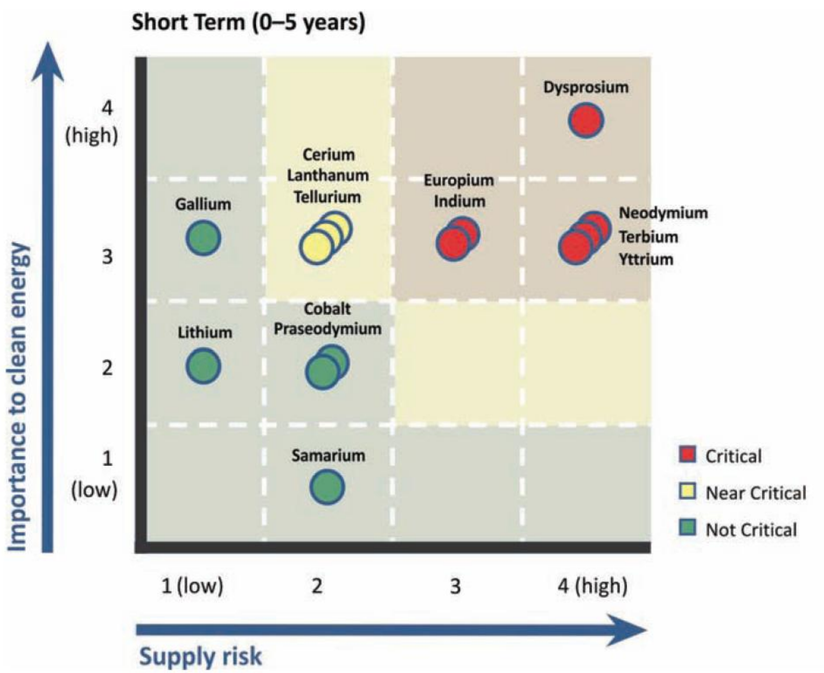
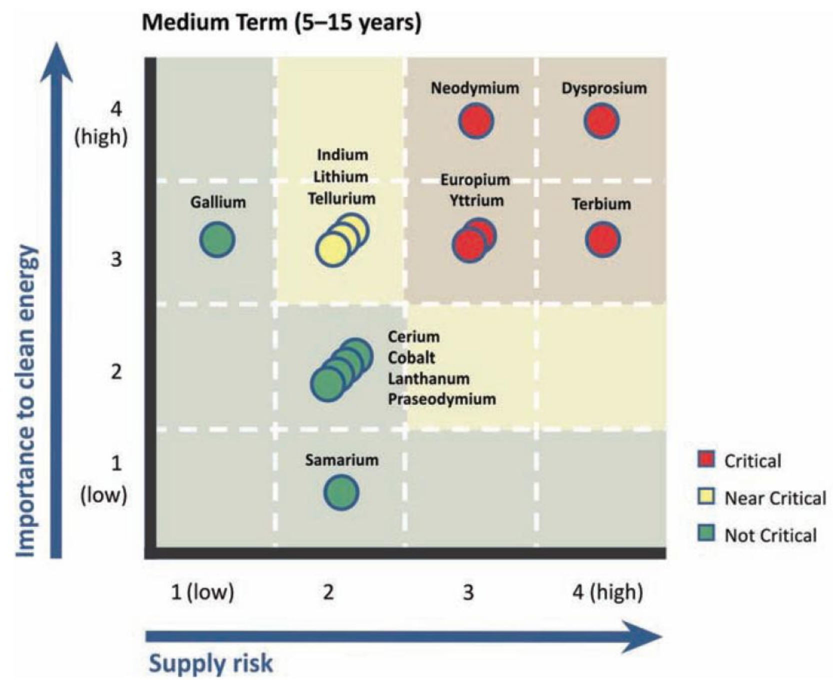
Rare earths are critical raw materials



Source: report EU commission "Critical raw materials for the EU" (2010)

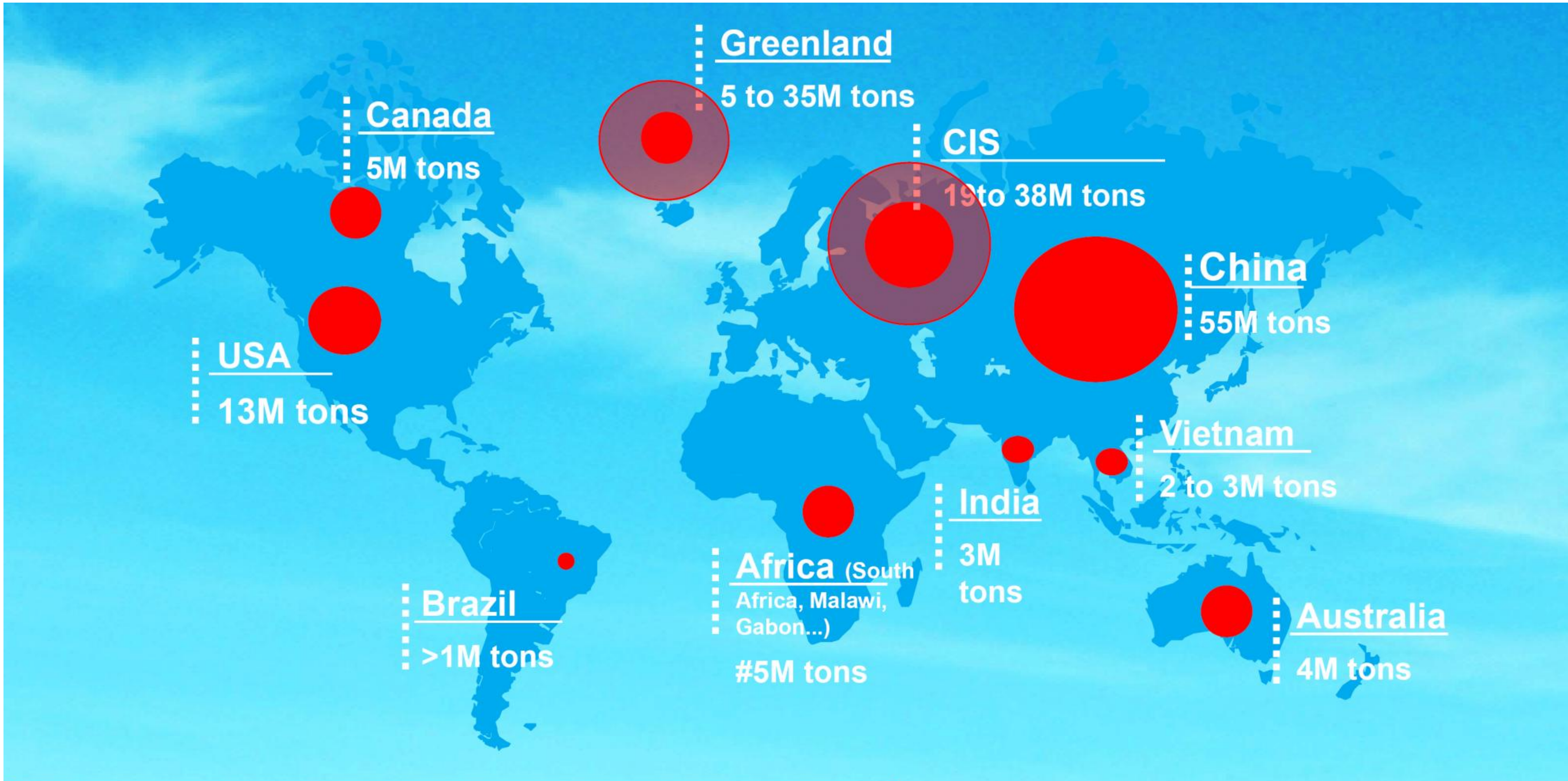
Suppy risk of rare earths





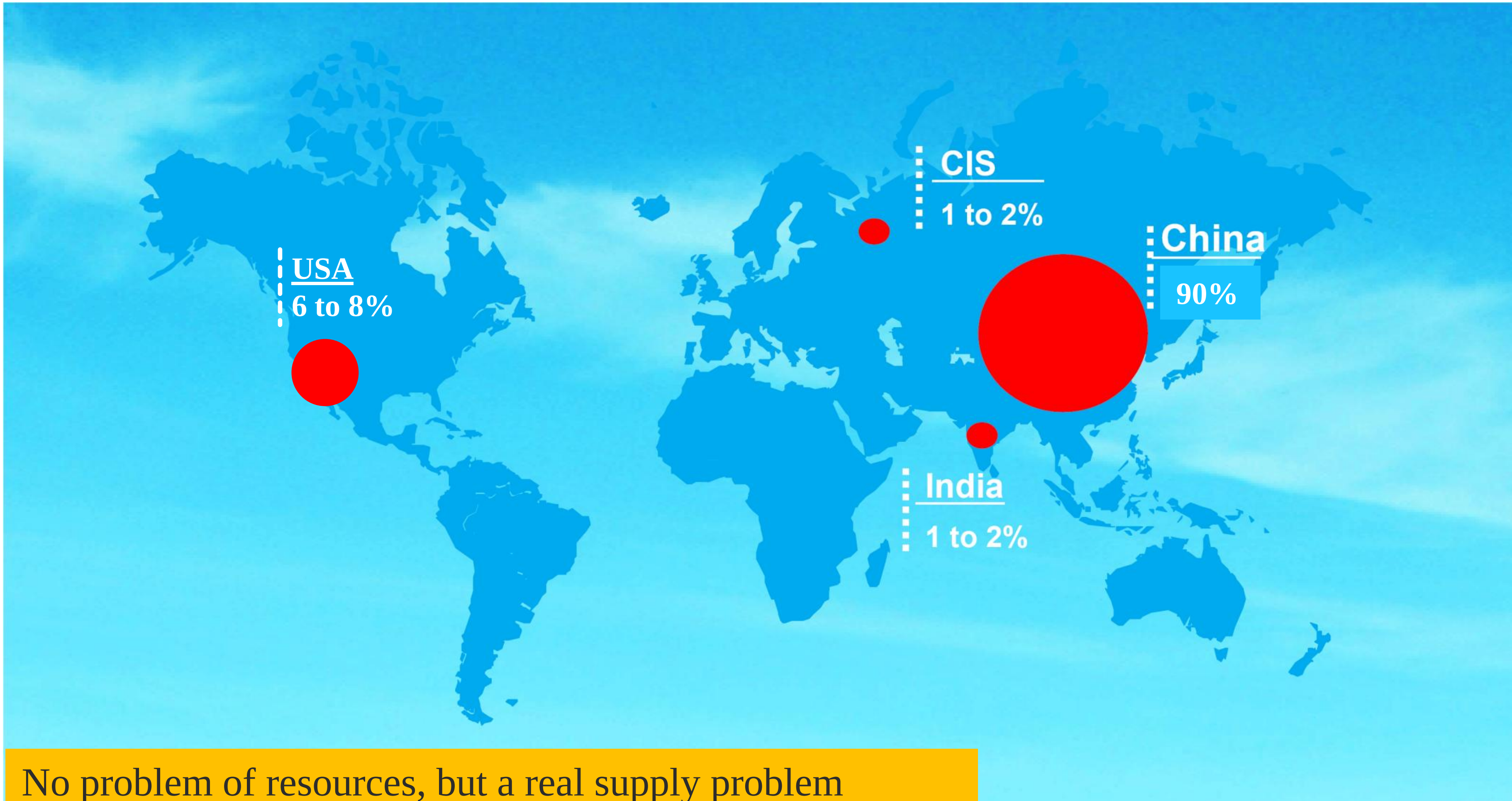
Source: report US Department of Energy(2010)

Global reserves are large and well distributed



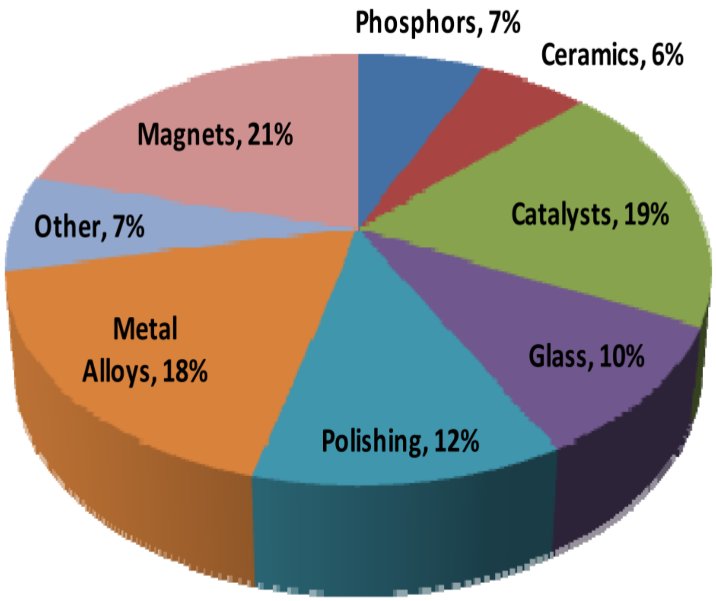
Reserves are at least 110 M t REO when the ww consumption is expected to be 150 kT REO in 2016

Production is largely concentrated in China (monopoly position)

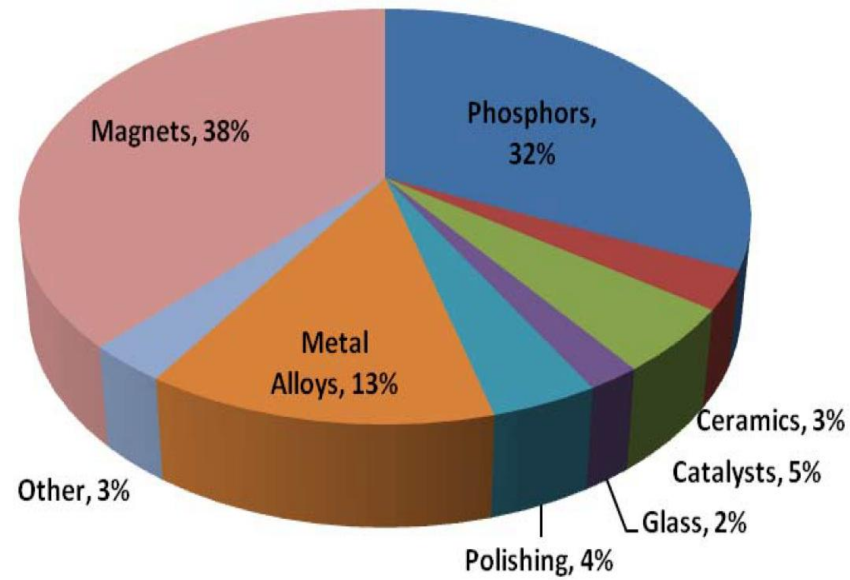


No problem of resources, but a real supply problem

Applications of rare earths



volume



value

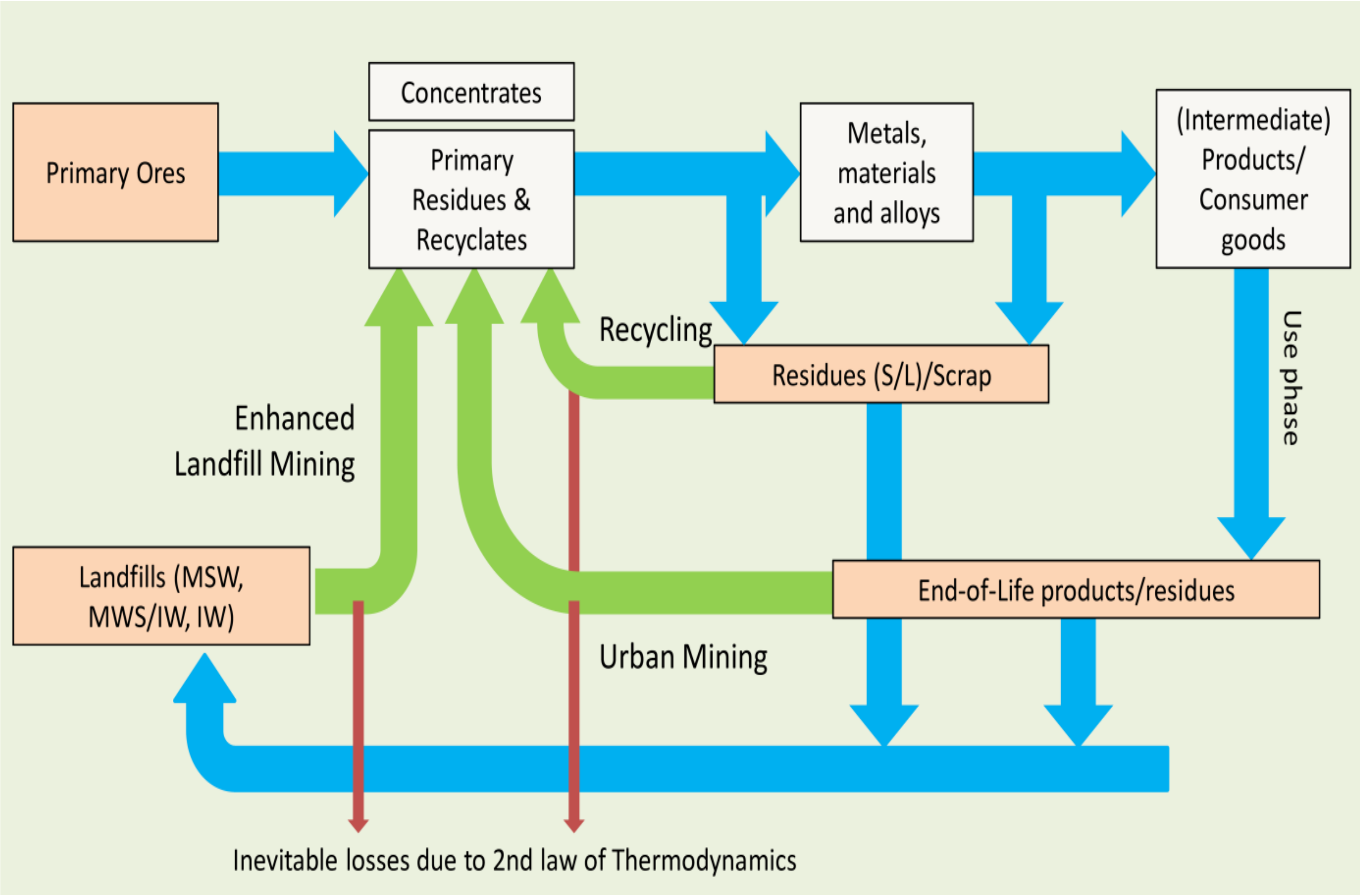
Total volume in 2012: 110,000 tonnes of REO

REEE usage by application

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powder	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

(source: Lynas Corporation)[8]

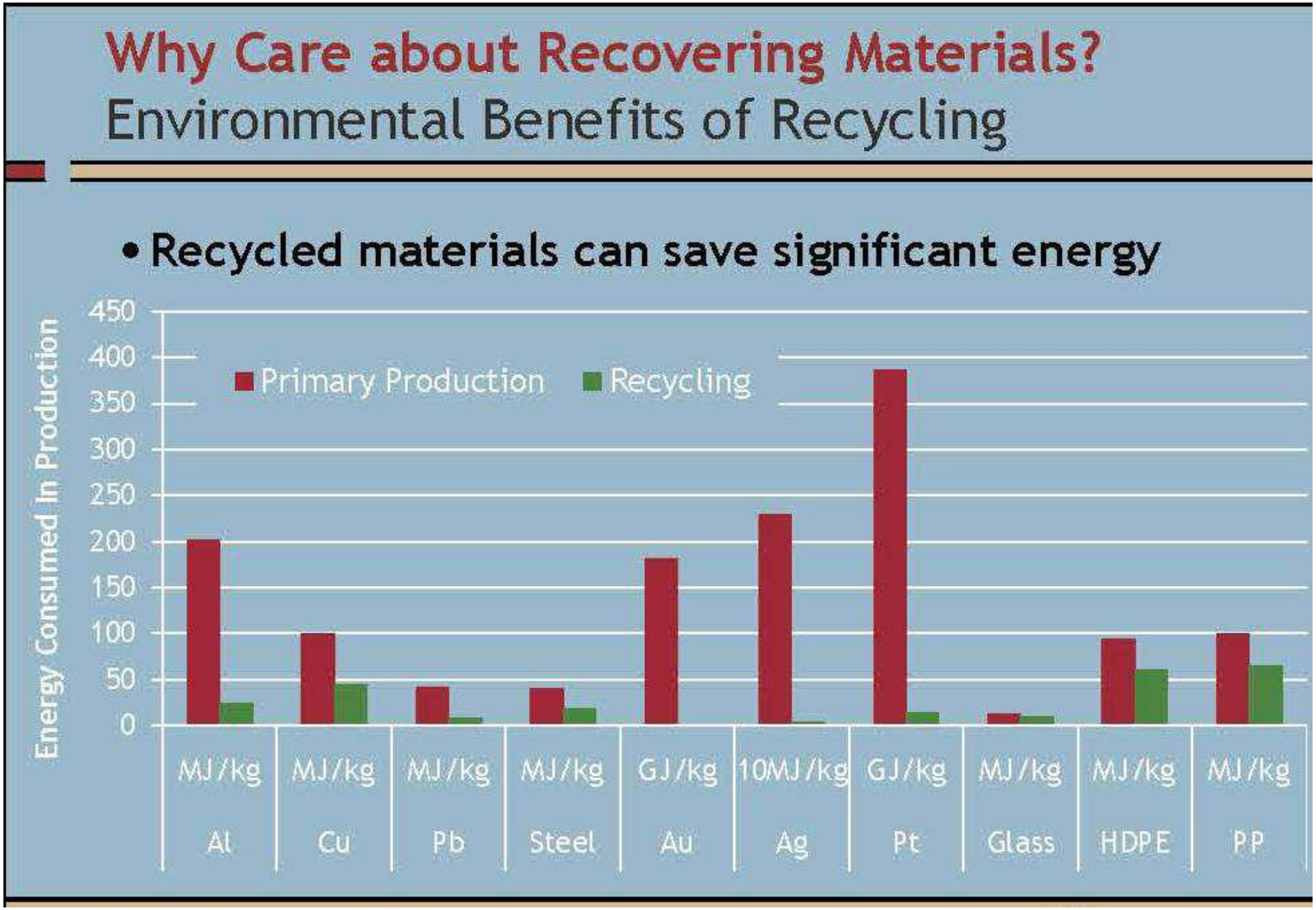
Recycling = closing the materials loop



Why recycling?

- Supply of critical raw materials
- Efficient use of natural resources
- Balance problem (specific for REEs)
- Extra advantage: no issues with radioactivity

Energy saving by recycling



Source: Diran Apelian, CR^3 presentation Leuven, 2010

Depletion of non-renawables

Table 2.4: predicted peak and depletion of different fuels and metals, and main area of usage.
Source: ITRE, March 2009

Commodity	Peak	Depletion	Main area of usage
Oil	2006-2026	2055-2100	Energy generation Chemical industry and pharmaceuticals Construction
Natural gaz	2010-2025	2075	Energy generation
Coal	2100	2160-2210	Energy generation
Antimony	-	2020-2035	Metal alloys
Copper	-	2040-2070	Energy transport Piping Electronics
Gallium	may have passed	-	Electronics (mobile phones, solar cells)
Indium	-	2015-2020	Electronics (LCDs, solar cells)
Lead	Passed	2030	Automobile industry Chemical industry
Platinium	-	2020	Electronics (printer, etc) Industry (plug, catalyser, glass production) Medicine (pacemaker)
Silver	-	2020-2030	Electronics Pharmaceuticals
Tantalum	-	2025-2035	Electronics (mobile phone, automobiles) Pharmaceuticals Chemical indusry
Uranium	-	2035-2045	Energy generation
Zinc	-	2030	Anticorrosives Energy storage

Balance problem

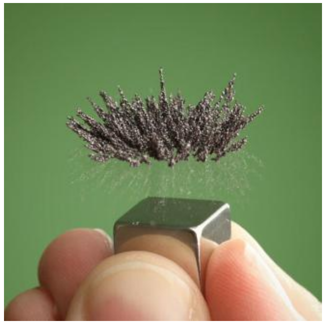
- **Balance problem** = demand and supply of the individual rare-earth elements (REEs) have to be equal at any time
- Also called: *Balancing problem*
- Became an issue when applications shifted from the use of mixed rare earths to pure rare earths
- Of importance for REE manufacturers
- Concept introduced by P. Falconnet (Rhone-Poulenc)
  J. Less-Common Metals 111 (1985) 9.

Early applications: mixed rare earths

- Mainly lanthanum and cerium
- **Catalyst industry**
    - Stabilization of zeolites for fluid cracking catalysts (FCC) during steam regeneration
- **Metallurgy (mischmetall)**
    - Graphite nodularization in cast iron
    - Ultimate desulfurization of steels
    - Lighter flints made of iron-mischmetall alloy
    - Grain growth inhibition in light metals
    - Battery alloys (NiMH)
- **Glass industry**
    - Polishing powder (CeO_2)

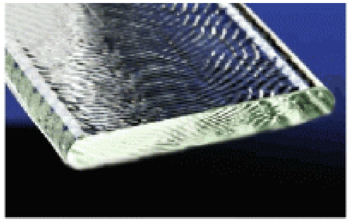
Modern applications: pure rare earths

- **Permanent magnets**
  - NdFeB (Nd,Pr,Dy)
  - SmCo (Sm)   (< 2% of market)



- **Phosphors**
  - Phosphors for trichromatic fluorescent lamps (Y, Eu, Tb, La, Ce)
  - Phosphors for CRTs (color television, computer monitors (Eu,Y)
  - X-ray intensifying screens (Gd,La,Tb)

- **Glass industry**
  - Optical glass (La)



REE content of selected minerals (%)

REE	Bastnasite Mountain Pass, USA	Bastnasite Bayan Obo, China	Monazite Mt. Weld, Australia	Xenotime Lehat, Malaysia	High Y RE laterite Longnan, China	Low Y RE laterite Xunwu, China	Loparite Kola Peninsula Russia
La	33.8	23.0	25.5	1.2	1.8	43.4	25.0
Ce	49.6	50.0	46.7	3.1	0.4	2.4	50.5
Pr	4.1	6.2	5.3	0.5	0.7	9.0	5.0
Nd	11.2	18.5	18.5	1.6	3.0	31.7	15.0
Sm	0.9	0.8	2.3	1.1	2.8	3.9	0.7
Eu	0.1	0.2	0.4	Trace	0.1	0.5	0.1
Gd	0.2	0.7	<0.1	3.5	6.9	3.0	0.6
Tb	0.01	0.1	<0.1	0.9	1.3	Trace	Trace
Dy	0.03	0.1	0.1	8.3	6.7	Trace	0.6
Ho	0.01	Trace	Trace	2.0	1.6	Trace	0.7
Er	0.01	Trace	Trace	6.4	4.9	Trace	0.8
Tm	0.01	Trace	---	1.1	0.7	Trace	0.1
Yb	0.01	Trace	---	6.8	2.5	0.3	0.2
Lu	Trace	Trace	---	1.0	0.4	0.1	0.2
Y	0.1	Trace	<0.1	61.0	65.0	8.0	1.3

Consequences of REE abundances

- To get 1 ton of Eu_2O_3 from bastnäsite, one needs to produce (and sell) the following amounts of REOs (tons):

La_2O_3	300
CeO_2	450
Pr_6O_{11}	38
Nd_2O_3	118
Sm_2O_3	7.3
Gd_2O_3	1.4
Y_2O_3	0.9

Ref.: P. Falconnet, Basic and Applied Aspects of Rare Earths, 1989 (Venice –Italy) p. 27

Balance problem

- Ideal situation: perfect balance between demand and production of all REE elements
- Market in balance corresponds to lowest price for any REE: production costs are shared by all elements
- Market in balance is very difficult to obtain, because of changes in demand by changes in applications
- Present light REE market is driven by demand for Nd for NdFeB magnets (about 25,000 tons in 2011)
- Sufficient quantities of REE ores have to be mined to produce at least 25,000 tons of Nd
- Ce, Pr, Sm are produced in excess (stockpiled)
- HREE market is smaller and mainly driven by Eu, Tb, Dy, Y

Recycling and the balance problem

- Recycling of NdFeB magnets to recover Nd and Dy means that less primary ores have to be mined to ensure supply of Nd and Dy
- Less mining means less over production of cerium, samarium, ...
- Recycling of Eu, Tb, Y from lamp phosphors helps to maintain the balance of HREE

Ref: K. Binnemans et al. JOM 65, 846–848 (2013)

Recycling of rare earths

- *Less than 1%* of the REEs were being recycled in 2011

  inefficient collection, technological issues, lack of incentives
- Main sources:
  - lamp phosphors (**Eu**, **Tb**, **Y**, Gd, La, Ce)
  - permanent magnets (**Nd**, Pr, Tb, **Dy**)
  - nickel metal hydride batteries (**La**, Ce) + Ni

Key reference

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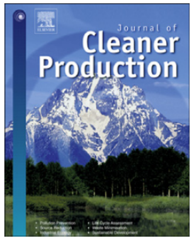

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Review

Recycling of rare earths: a critical review

CrossMark

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Lamp phosphors

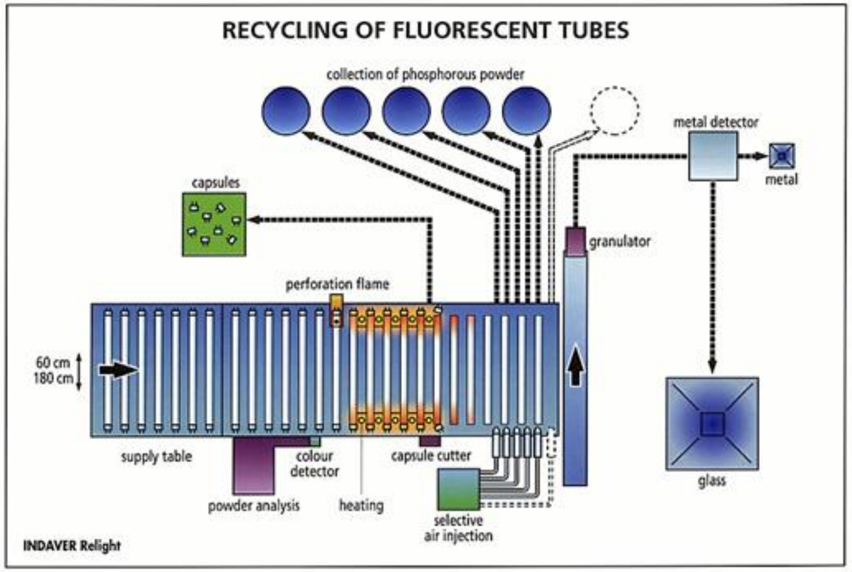
Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

Different options for recycling of lamp phosphors

- Direct re-use
- Separation of phosphors in individual components
- Recovery of REE content

Direct re-use of lamp phosphors

- Advantages
  - Very simple method
  - No chemical processing required
- Disadvantages
  - Only applicable to one type of fluorescent lamps, because different lamps make use of different phosphor mixtures
  - Phosphors deteriorate over the lifetime of the lamp



Separation of phosphors in individual components

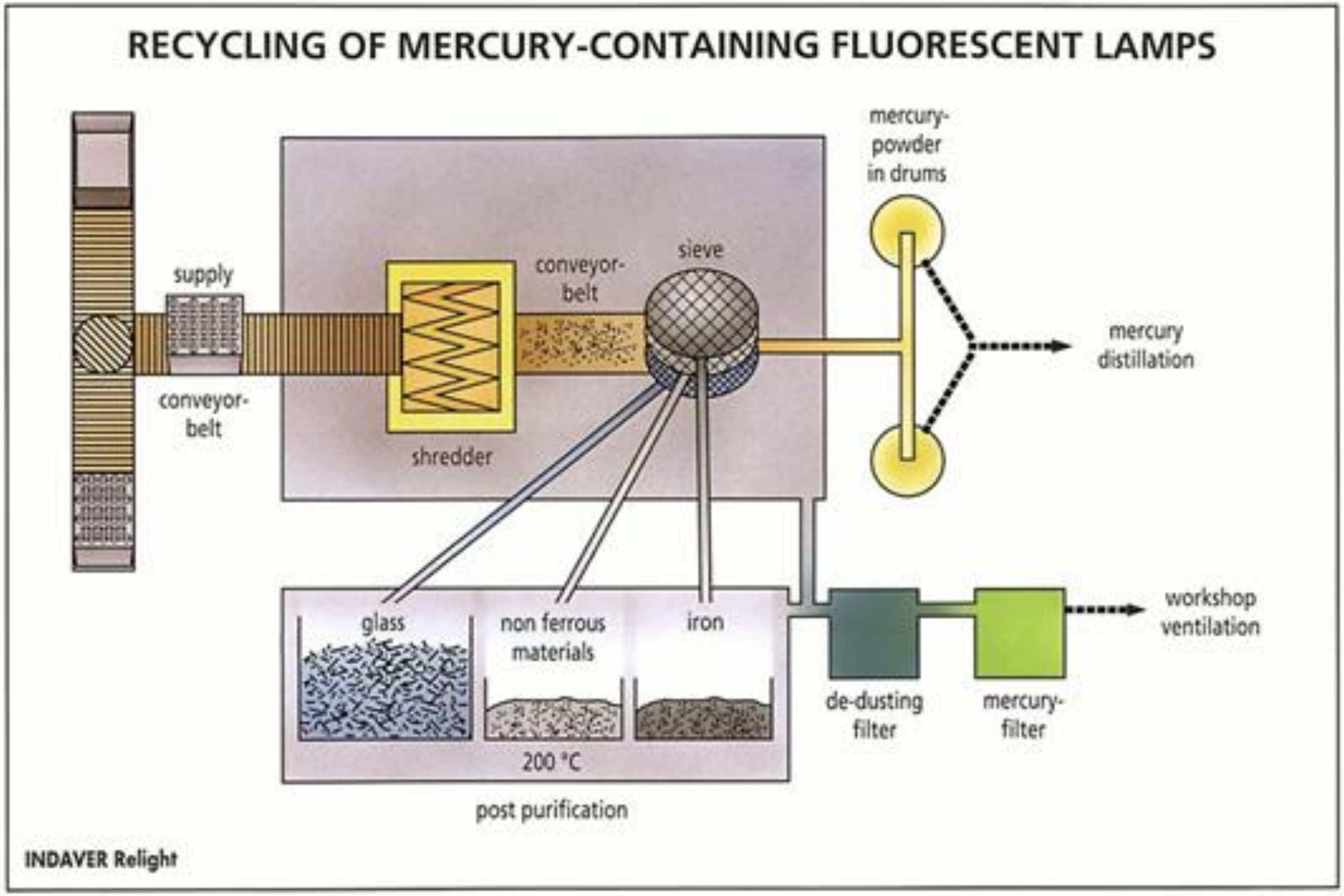
- Advantages:
  - Relatively simple process
  - No or limited amounts of chemicals are consumed
- Disadvantages:
  - Very difficult to obtain very pure phosphor fractions
  - Separation process may change the phosphor particle size
  - Phosphors deteriorate over the lifetime of the lamp

- Techniques:
  - Flotation
  - Pneumatic separation
  - Gravity separation in a dense medium

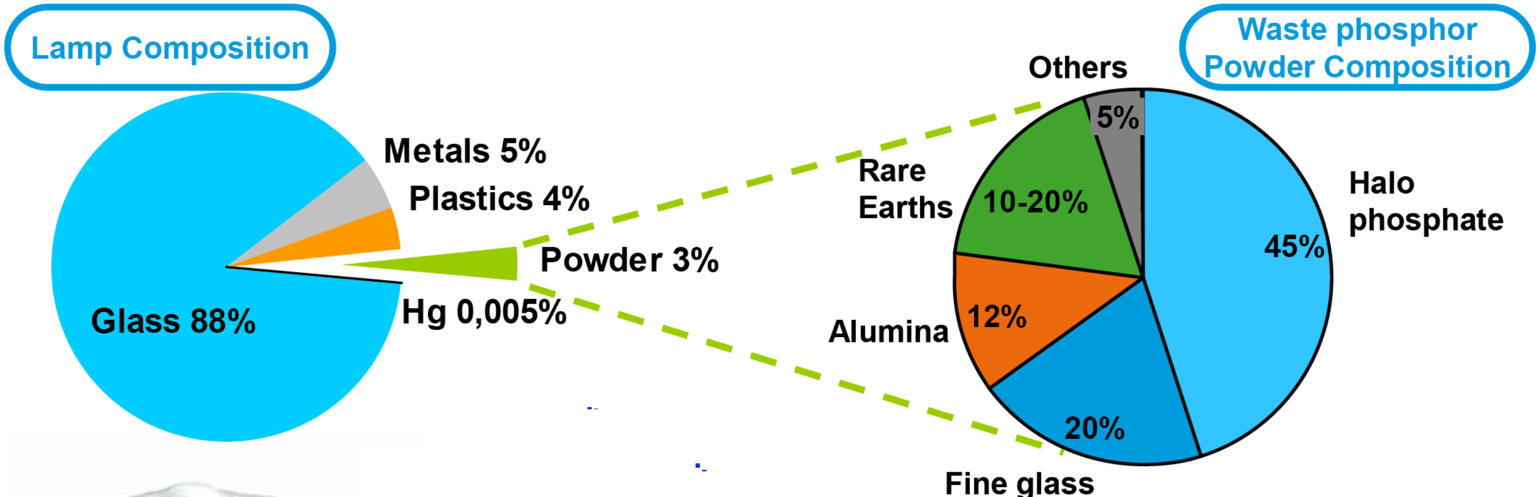
Recovery of REE content

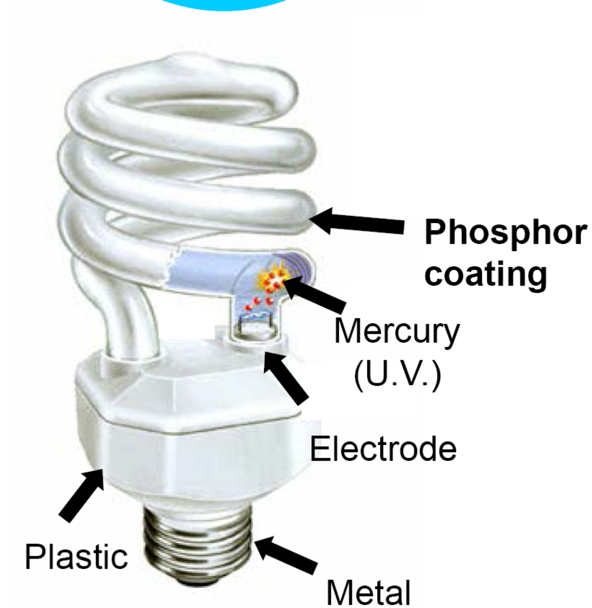
- Advantages:
  - Generally applicable to all types of phosphor mixtures
  - Same processing steps as those used for extraction of rare earths from primary ores (acid and alkali attack of phosphors)
  - Gives very pure rare-earth oxides that can also be used for other applications
- Disadvantages:
  - Many process steps required before obtaining new lamp phosphors
  - Consumption of large amounts of chemicals
  - Generation of large amounts of waste water

Crushing and sieving of fluorescent lamps



Composition of waste lamp phosphor fraction





RE based phosphors

BAM $BaMgAl_{10}O_{17}:Eu^{2+}$

YOX $Y_2O_3:Eu^{3+}$

LAP $(La,Ce)PO_4:Tb^{3+}$

CAT $CeMgAl_{10}O_{19}:Tb^{3+}$

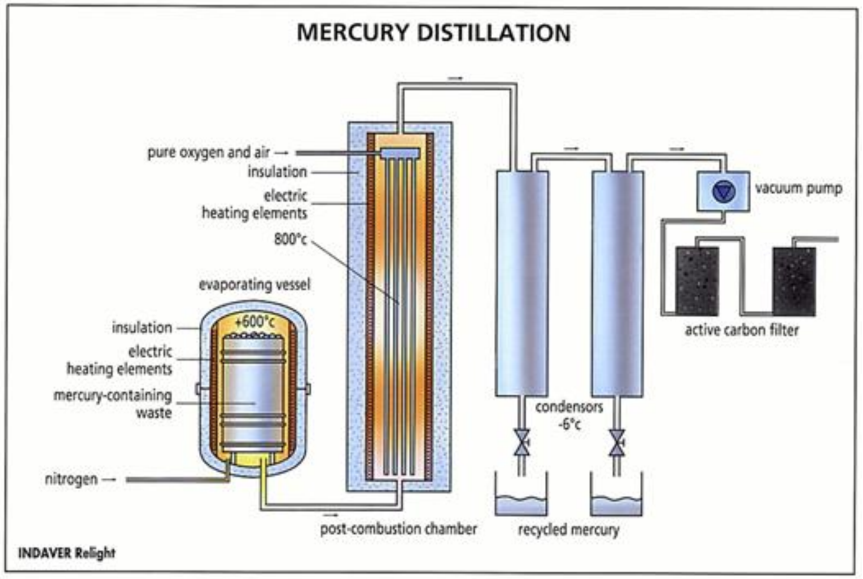
Rhodia
Member of the Solvay group

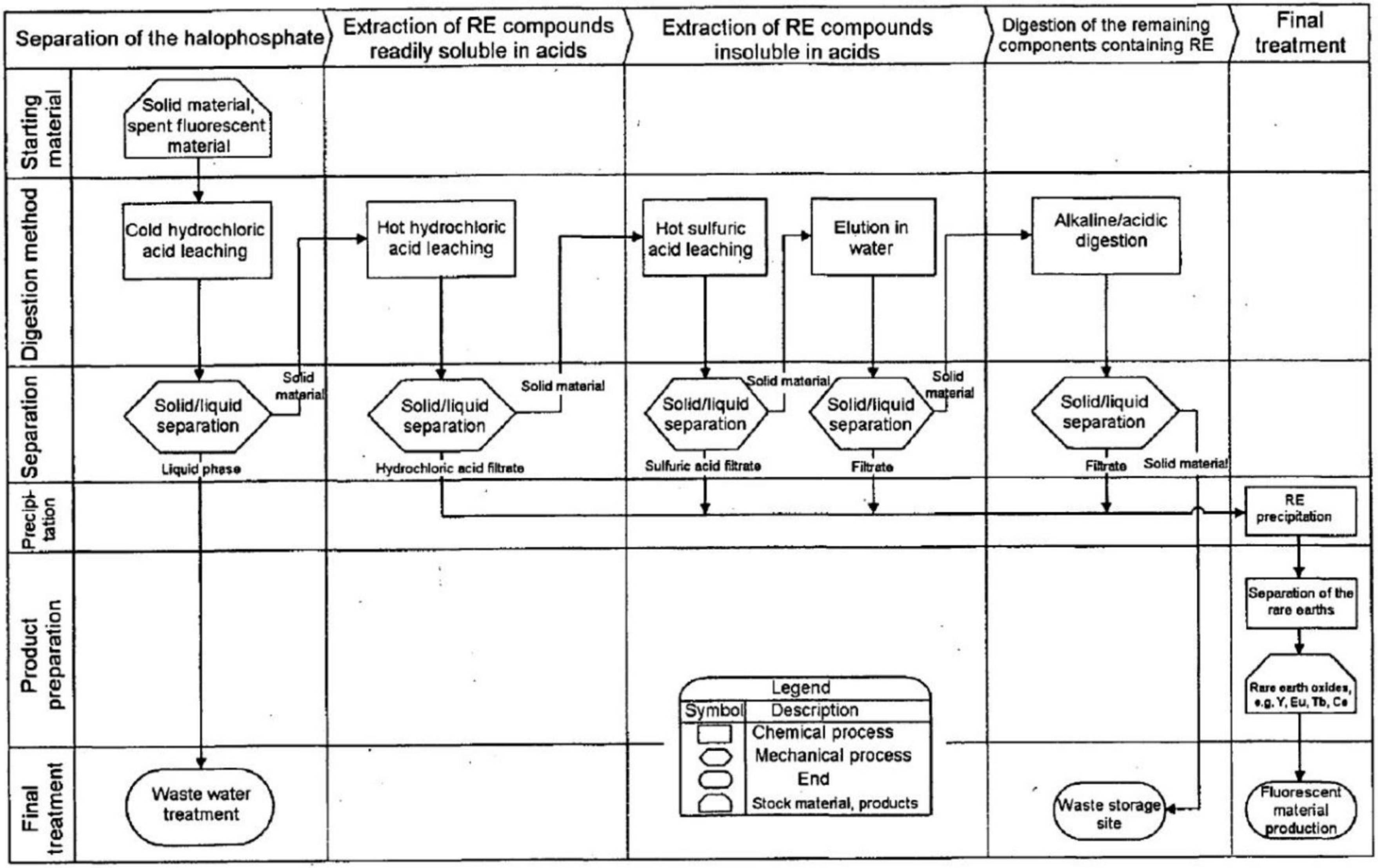
Removal of mercury

- Mercury removal is an issue closely related to the recycling of REEs from lamp phosphors (environmental hazard)
- The mercury content of fluorescent lamps varies widely depending on type of lamp (linear tubes versus compact fluorescent lamps), the brand, the wattage and the year of manufacturing.
- General trend is a steady decrease in mercury content over the years due to more strict environmental laws
- Since 2012, compact fluorescent lamps with a power lower than 50 W are not allowed to contain more than 3.5 mg Hg/lamp, according to EU regulations
- For compact fluorescent lamps, more than 85% of Hg ends up in the phosphor layer when the lamp reaches the end of its lifetime
- Hg is a problem for recycling of REE from lamp phosphors, but Hg made efficient collection of end-of-life fluorescent lamps possible

Removal of mercury

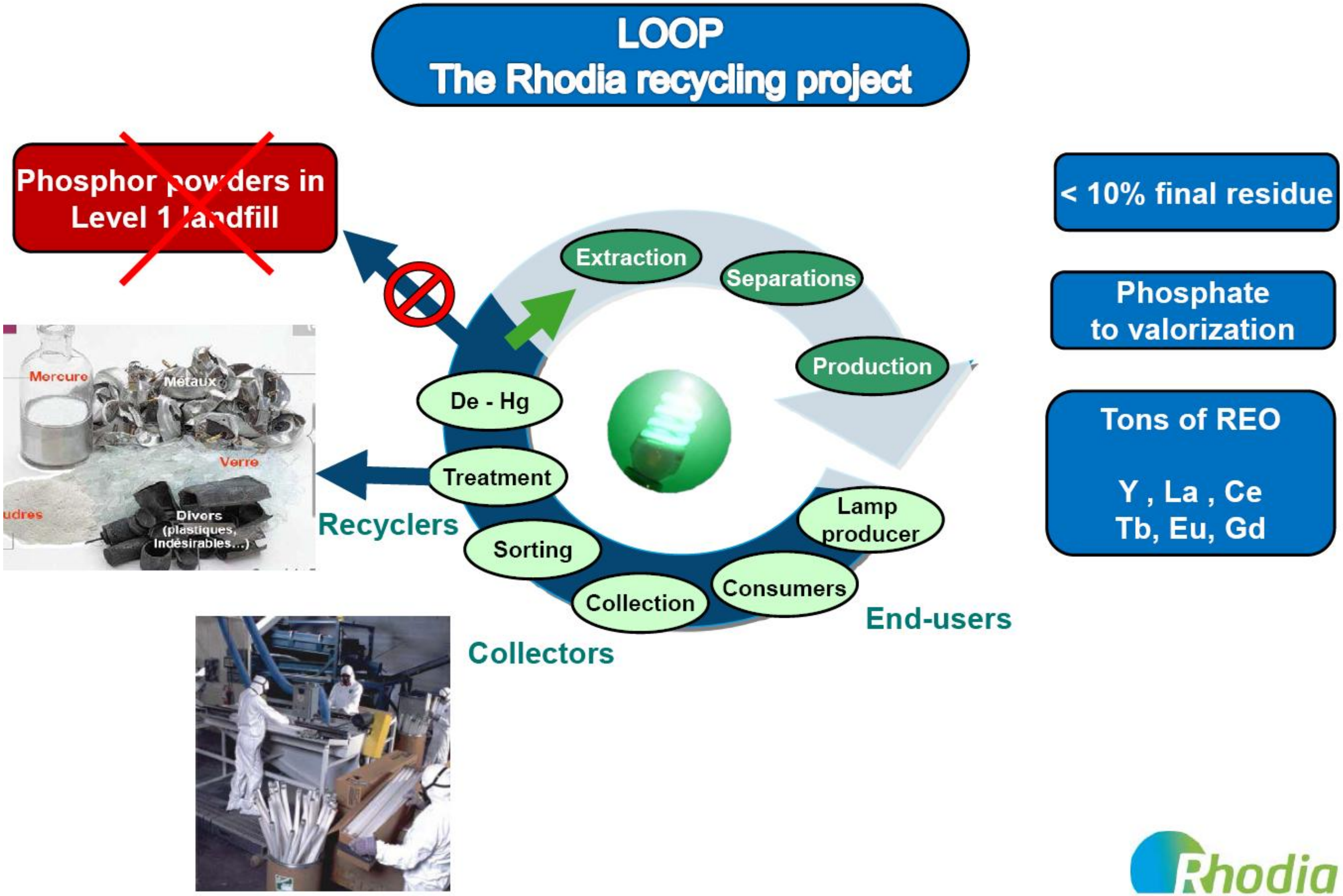
- Thermal treatment of the phosphor mixture for several hours at 400-600 °C in vacuum removes larger part of Hg
- full removal of Hg is only possible by heating the phosphor powder to at least 800 °C
- very energy-consuming and cannot be used when wet sieving procedures are being applied to separate the phosphors from glass and metallic parts in crushed fluorescent lamps.





Ref.: Otto, R., Wojtalewicz-Kasprzac, A., 2012. Method for Recovery of Rare Earths From Fluorescent Lamps. US Patent 2012/0027651 A1

Rhodia Solvay's lamp recycling project



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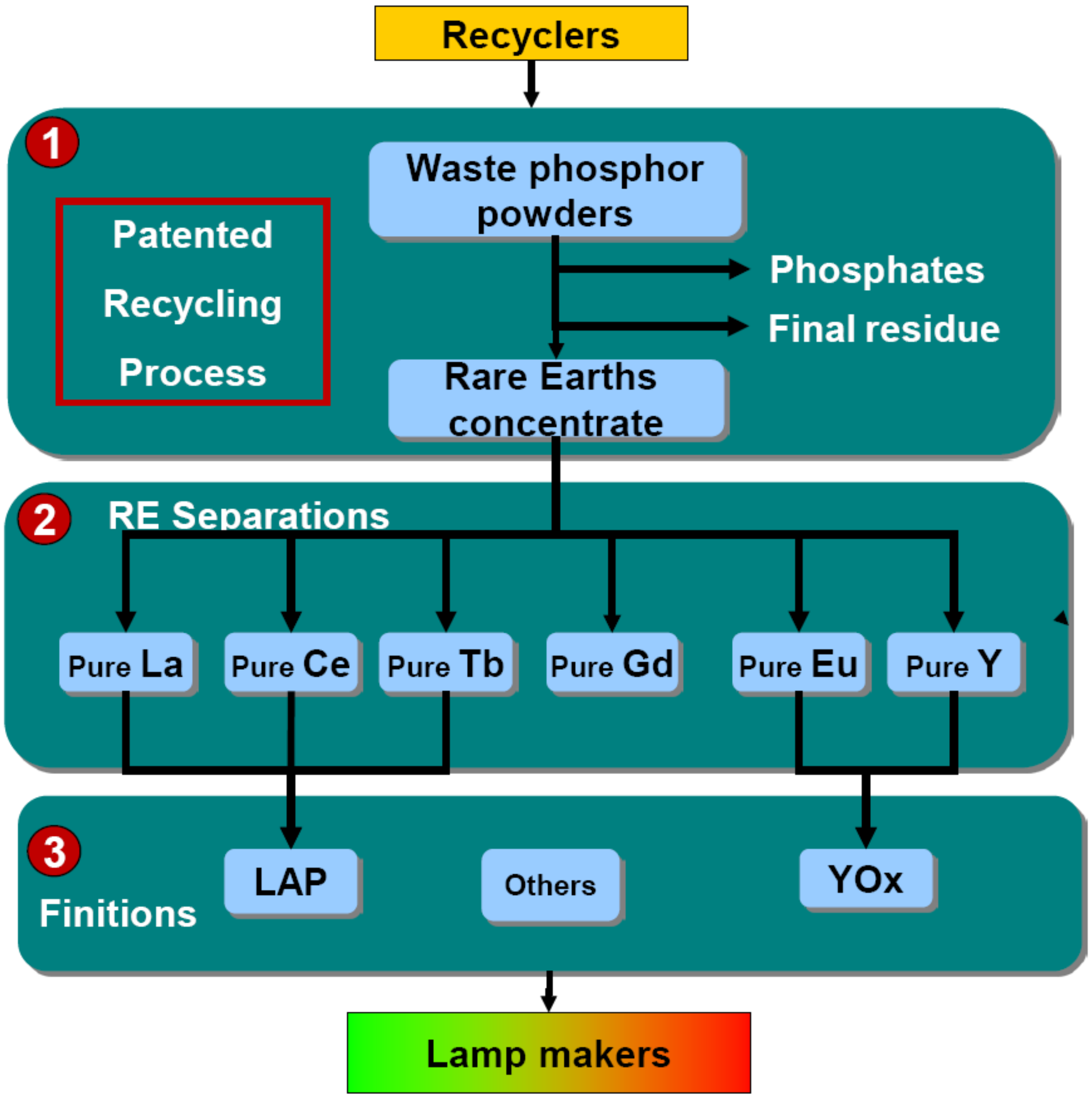
Rhodia Solvay's lamp recycling project



<u>A 3 steps process</u>

1. Rare Earth extraction (La,Ce,Y,Eu,Tb,Gd)

Saint Fons

La Rochelle

2. Rare Earth Separations

La Rochelle

3. Production of YOX (red) & LAP (green) & others

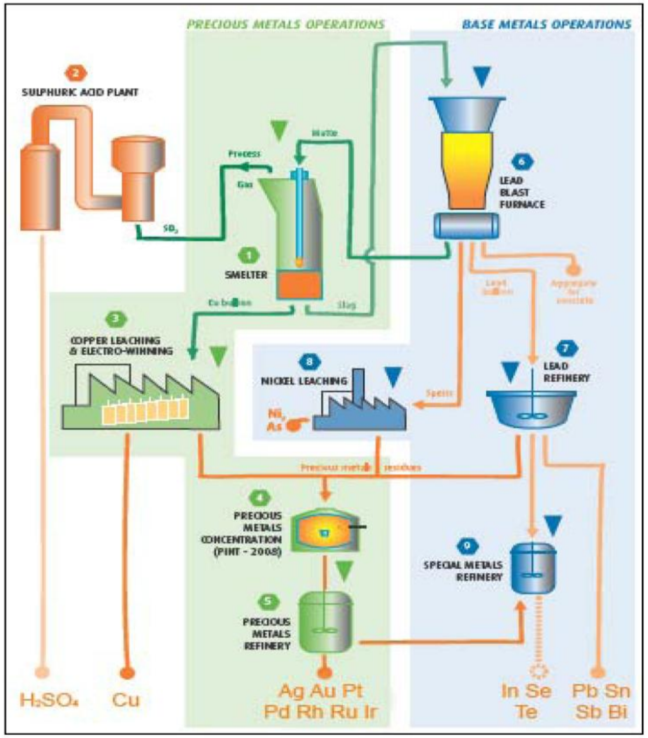
La Rochelle

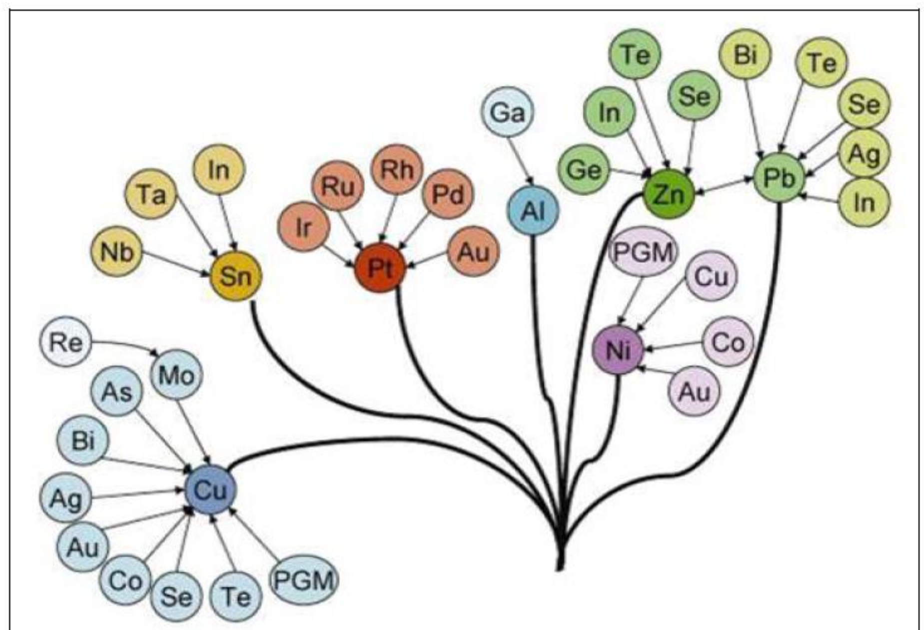
Rhodia
Member of the Solvay group

Recycling of REE from NdFeB magnets

- Main focus on NdFeB magnets (98-99% of the market)
  Topic of MC-ITN "European rare-earth magnet recycling network" (**EREAN**)
- During pyrometallurgical recycling of metals from electronic scrap and used catalysts, they end up as oxides in slags. Concentration in oxide slags is too low for recycling
- In many applications, the amount of REE per item is low (a few grams), so that deep-level dismantling is recommended to recover REE-containing objects.
- Dismantling can be automated (e.g. Hitachi)

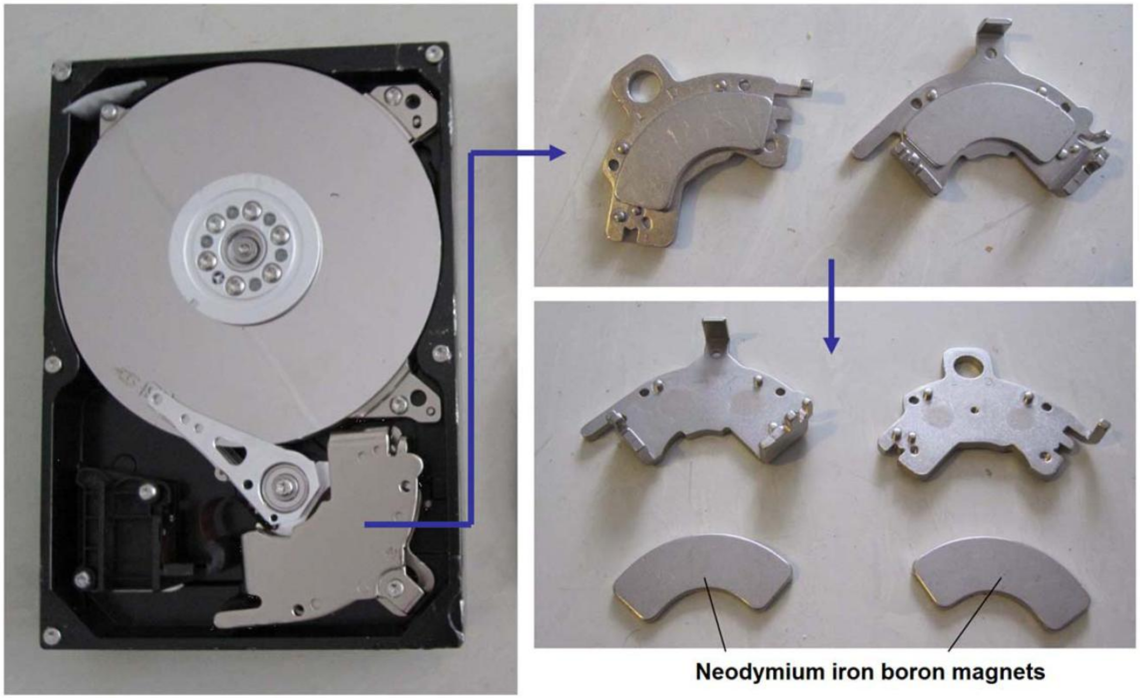
Umicore's metal recycling plant (Hoboken, Belgium)





- REEs lost to oxide slags (low concentration)
- slags used as building material

Amounts of rare earths in electronic devices

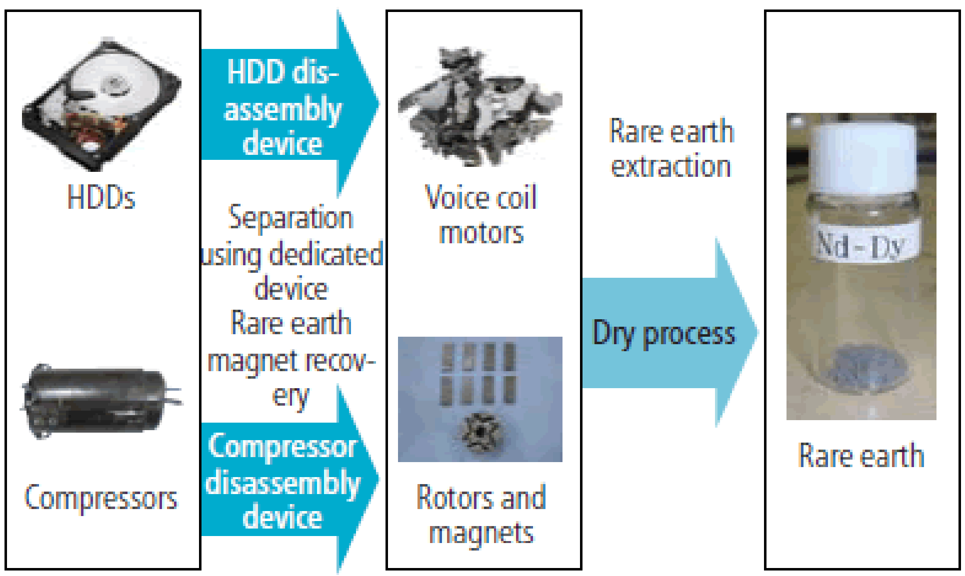


Magnets: 2 wt.% of HDD
REE: 0.6 wt.% of HDD

Source: Öko-Institut

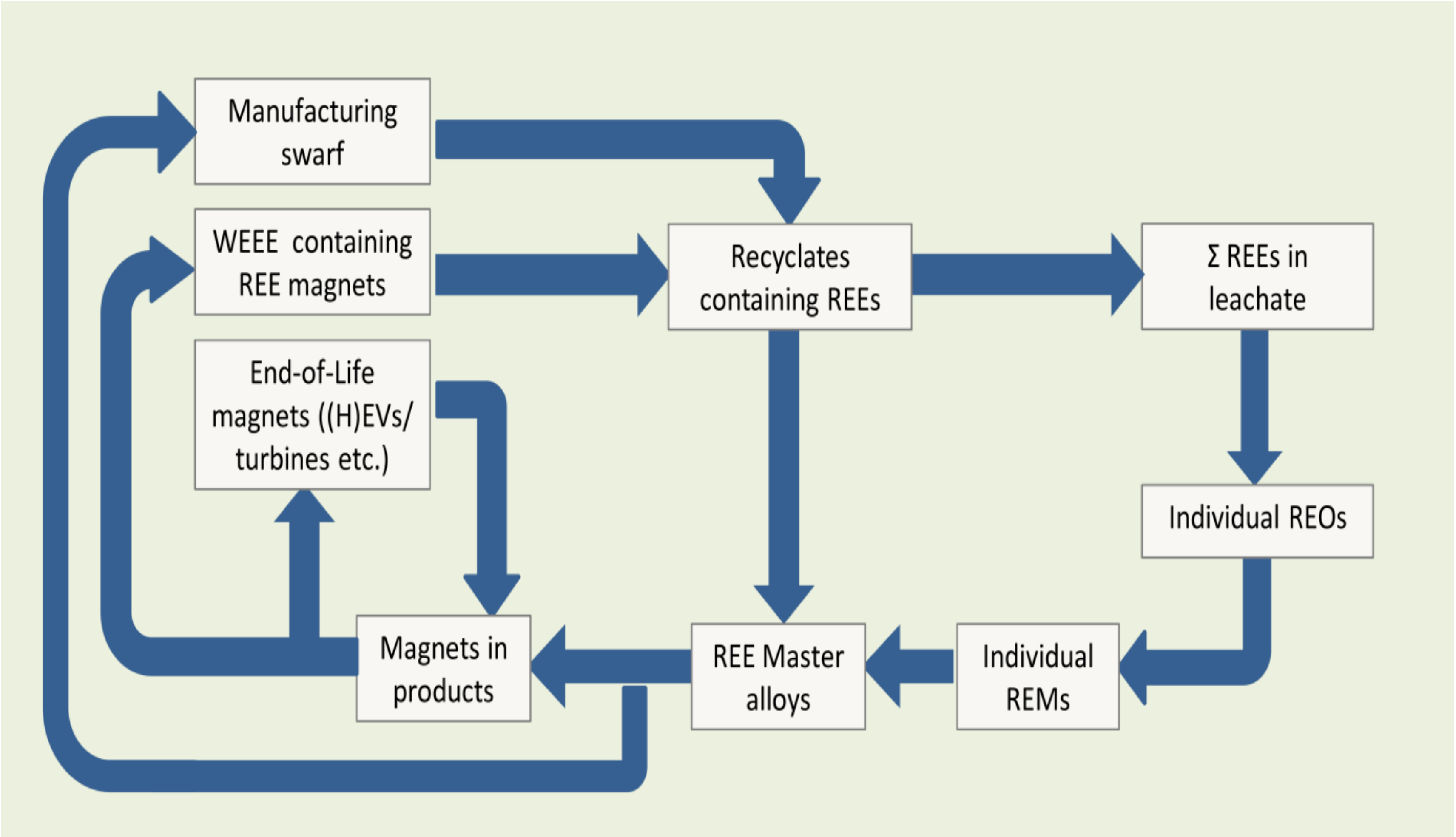
Mobile phones: only 0.1 to 0.25 g of REEs

Dismantling by Hitachi



Source: Hitachi

Flow sheet for recycling of magnets



Different options for recycling of magnets

- Direct re-use in current form/shape
- Reprocessing of alloys to magnets after hydrogen decrepitation
- Hydrometallurgical methods
- Pyrometallurgical methods
- Gas-phase extraction

Direct re-use in current form/shape

- Advantages:
  - Most economical way of recycling (low energy input, no consumption of chemicals)
  - No waste generated
- Disadvantages:
  - Only for large easily accessible magnets (wind turbines, large electric motors and generators in hybrid and electric vehicles
  - Not available in large quantities in scrap today

Reprocessing of alloys to magnets after hydrogen decrepitation

- Advantages
  - Less energy input required than for hydrometallurgical and pyrometallurgical routes
  - No waste generated
  - Especially suited for hard disk drives (little compositional change over the years)
- Disadvantages
  - Not applicable to mixed scrap feed, which contains magnets with large compositional variations
  - Not applicable to oxidized magnets

Hydrometallurgical methods

- Advantages
  - Generally applicable to all types of magnet compositions
  - Applicable to non-oxidized and oxidized alloys
  - Same processing steps as those for extraction of rare earths from primary ores
- Disadvantages
  - Many process steps required before obtaining new magnets
  - Consumption of large amounts of chemicals
  - Generation of large amounts of waste water

Pyrometallurgical methods (liquid metal extraction)

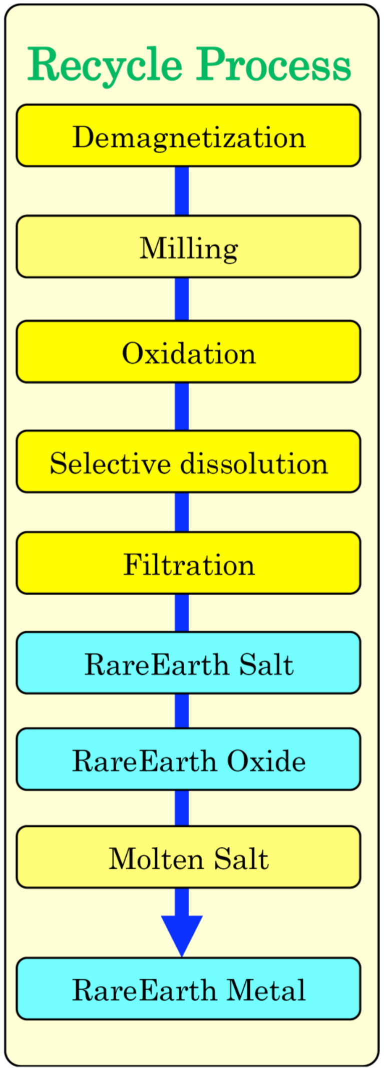
- Advantages
  - Generally applicable to all types of magnet compositions
  - No generation of waste water
  - Fewer processing steps than hydrometallurgical methods
  - Direct melting allows obtaining master alloys
  - Liquid metal extraction allows obtaining REEs in metallic state
- Disadvantages
  - Larger energy input required
  - Direct smelting and liquid metal extraction cannot be applied to oxidized magnets
  - Electroslag refining and the glass slag method generate large amounts of solid waste

Gas-phase extraction

- Advantages
  - Generally applicable to all types of magnet compositions
  - Applicable to non-oxidized and oxidized alloys
  - No generation of waste water
- Disadvantages
  - Consumption of large amounts of chlorine gas
  - Aluminum chloride is very corrosive

Magnet recycling by SANTOKU

- SANTOKU Corporation has opened in 2012
- a plant in Tsuruga (Japan) for recycling Nd and Dy from magnets
  - Motor magnets (air conditioners)
  - Magnet production scrap
- Demagnetization by heating (6 hours at 573 K)
- Milling under 75 micron by jaw crusher and pulverizer
- Oxidation by stirring for 12 hours in an alkaline solution
- Selective dissolution in HCl
- Magnet alloys prepared by molten salt electrolysis



Source: SANTOKU

Different options for recycling of NiMH batteries

- Hydrometallurgical routes
- Pyrometallurgical routes

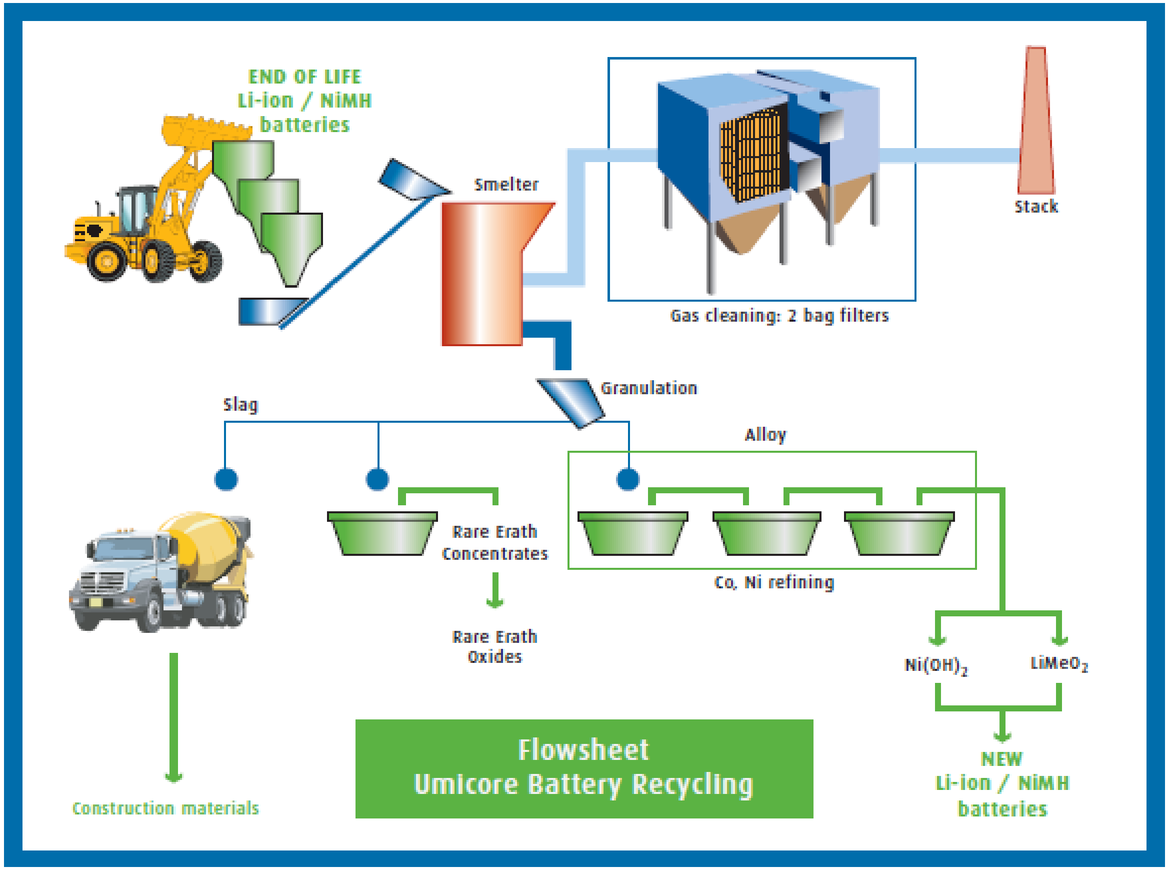
Hydrometallurgical routes

- Advantages
  - Low investment costs
  - Recycling possible of different waste fractions (cathode and anode materials, metals from casing) that can be marketed separately
- Disadvantages
  - Many manual operations are required for dismantling of batteries and separating the different components
  - Large consumption of chemicals

Pyrometallurgical routes

- Advantages
  - Well-developed technology
  - Energy recovery from plastic casings and other organic components
  - Same processing steps used for extracting REEs from slags as from primary ores
- Disadvantages
  - High investment cost for furnace
  - REEs need to be extracted from slags
  - REEs are obtained as mixtures and further separation is required

Recycling process for NiMH/ Li-ion batteries @Umicore



Source: Maurits van Camp (Umicore)

Recycling process for NiMH/ Li-ion batteries @Umicore

- Process developed for NiMH batteries
  - First industrial scale process
- Co-operation with Solvay Rhodia
  - Umicore produces REE-concentrate
  - Umicore separates REO from harmful elements
  - Solvay Rhodia refines REE concentrate
  - For EOL Portable NiMH batteries only
- Process of recovery of REE is not compatible with process of recovery PGM from exhaust catalysts

Conclusions

- Recycling cannot replace primary mining of REE ores, but complements mining
- Recycling of REEs is recommended for:
  - Efficient use of natural resources
  - Supply of critical raw materials
  - Balance problem
- Most interesting waste streams for REE recycling:
  - Lamp phosphors
  - NdFeB magnets
  - NiMH batteries
- REE recycling is technologically challenging, but not impossible

rare3

Research Platform for the
Advanced Recycling and Reuse of Rare Earths

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Thank you!